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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. §1.53(b)(2)

Atty. Docket: MAGDASSI1

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[ ] Additional inventors are being named on separately numbered sheets attached hereto

TITLE OF THE INVENTION (280 characters max)

DGP- DIGITAL GLASS PRINTER

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ENCLOSED APPLICATION PARTS (check all that apply)

[X] Specification — Number of Pages 16 — [X] Applicant claims small entity status. See 37 C.F.R. §1.27

[X] Drawing(s) — (Incorporated in specification) — [ ] Other (specify) ____________

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Respectfully submitted,

BROWDY AND NEIMARK, P.L.L.C.

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RLB:jlu

PATENT APPLICATION SERIAL NO. ____________________

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DGP – Digital Glass Printer
Provisional Application for Patent

I. Background of the invention

The silk printing machine that is used today to print on flat safety glass carries several disadvantages:

- Long set-up time in shifting from one series to another
- High workforce, production, materials and storage costs
- Difficulties to meet unique customer's requirements (color, size, shape, small production series etc.)
- High overall costs and lack of flexibility

The purpose of the invention is to replace the traditional silk printing machine used in the flat safety glass industry with a digital format printer which uses an inkjet ink. The ink becomes an integral part of the glass, in an industrial process, which includes heating over 600°C after the printing.

Digital Glass printing solves the above-mentioned disadvantages of silk printing.

The invention can be utilized for the following purposes that are served today by silk printing:

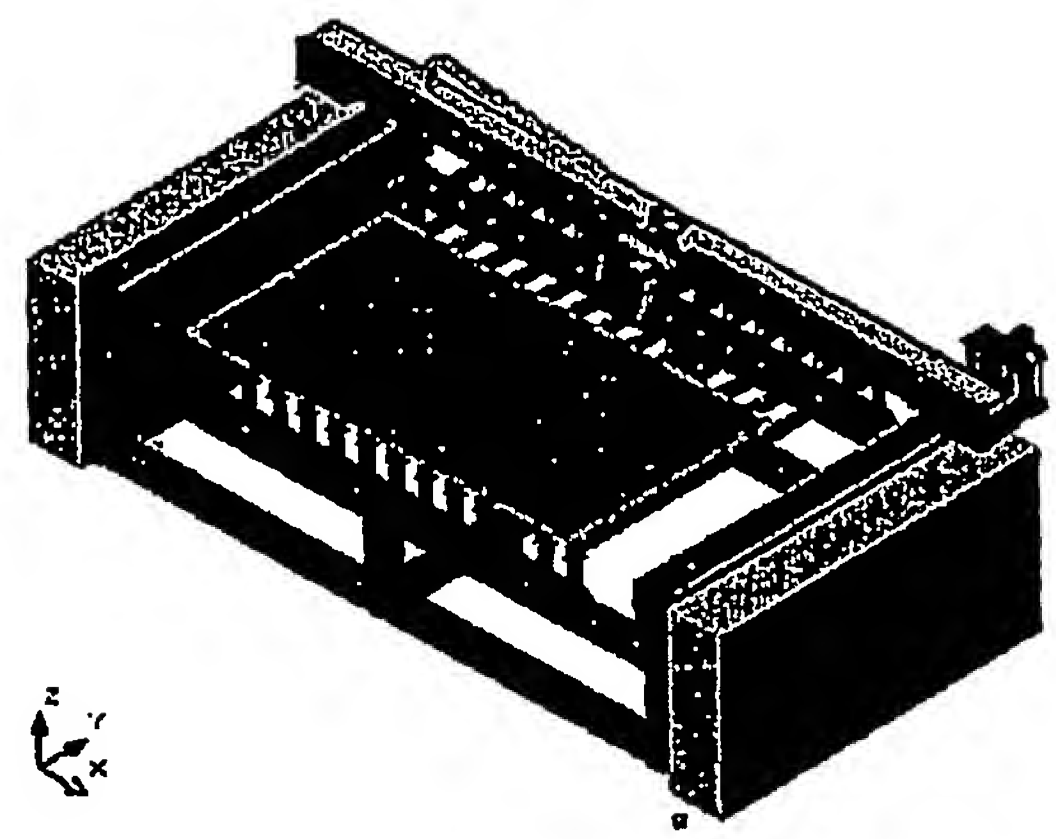
1. Automotive: vehicle's windscreens and windows have a thin painted pattern (a frame) around their upper part, which protects the glue that attaches the window to the car from the UV radiation and decorates the windscreen.
2. Architecture: decorative windows for internal and external uses.
3. Home Appliances: windows for microwave ovens, ovens, refrigerators (the invention is not limited to wide format printing).

In order to achieve the requirements of such printed patterns, which are far different from those of conventional printing (for example, for an automotive windscreens: very high temperature durability, above 600°C, resistance to soaking in warm sulfuric acid and sodium hydroxide solutions etc.), it is essential to develop both a printing machine, and an ink which will function in this printer.

Therefore, below we describe both the machine features, and the inks systems, which were invented in order to obtain the required digital glass printing.

II. The Printing machine

An industrial large format digital inkjet printer for printing glass based ink on safety glass, such as for the automotive OEM (Original Equipment Manufacturer), ARG (Automotive Replacement Glass), Architecture and Appliances markets.



General description

The printing machine includes three sections:
1. The inlet and positioning module
2. The printing module
3. The outlet module

All the sections from the inlet through printing and outlet perform simultaneously by double handling (while in feeding new glass for printing, the former printed glass is taken out of the machine)

The invention is the first system, based on Hydraulic and Electro-Mechanic elements, that enables digital printing on Glass and also handles, inter alia, the following:
- The ink can be jetted
- Heating
- Circulation
- Screening
- Pressures
- Prevention of sinking of the particles
- Operating Temperature
- Ink drying after jetting

1. The inlet and positioning unit

The glass is positioned in exact position through a system of servo-controlled axes or laser pointed location pins. Once the glass was located at a known and a precise location it is held by vacuum suction cups and is being fed precisely into the printing section.

2. Printing section

The printing section is a flat bed gantry type machine with 4 precise axes X, Y, Y, K (double Y axis) with the following assemblies:

1. Print head module
2. Ink system
3. Printing axis (X)
4. Advancing axis (Y,Y)
5. Vacuum system
6. Drying/Curing system (Curing refers to UV ink which might be also an option)
7. Software.

The process in the printing section contains the following: glass handling, glass printing in the fastest method, glass drying.

2.1 Print head module

The print head module consists of print head array, flushing manifold, head heating system.

2.2 Ink system handling

The ink contained large dense inorganic particles (frit), thus inks may need special care and handling via agitation systems and re-circulation from the main tank to the mid tank and re-circulation in the mid-tank all in order to prevent performance being adversely affected by settling and finely clogging of the print heads nozzles.
In addition, an automatic flashing system will be developed in order to increase the print heads endurance.

2.3 Printing axis

Developing the ability to print in both axis X and Y by rotating the print head module (All printing devices deal with printing in one axis only).

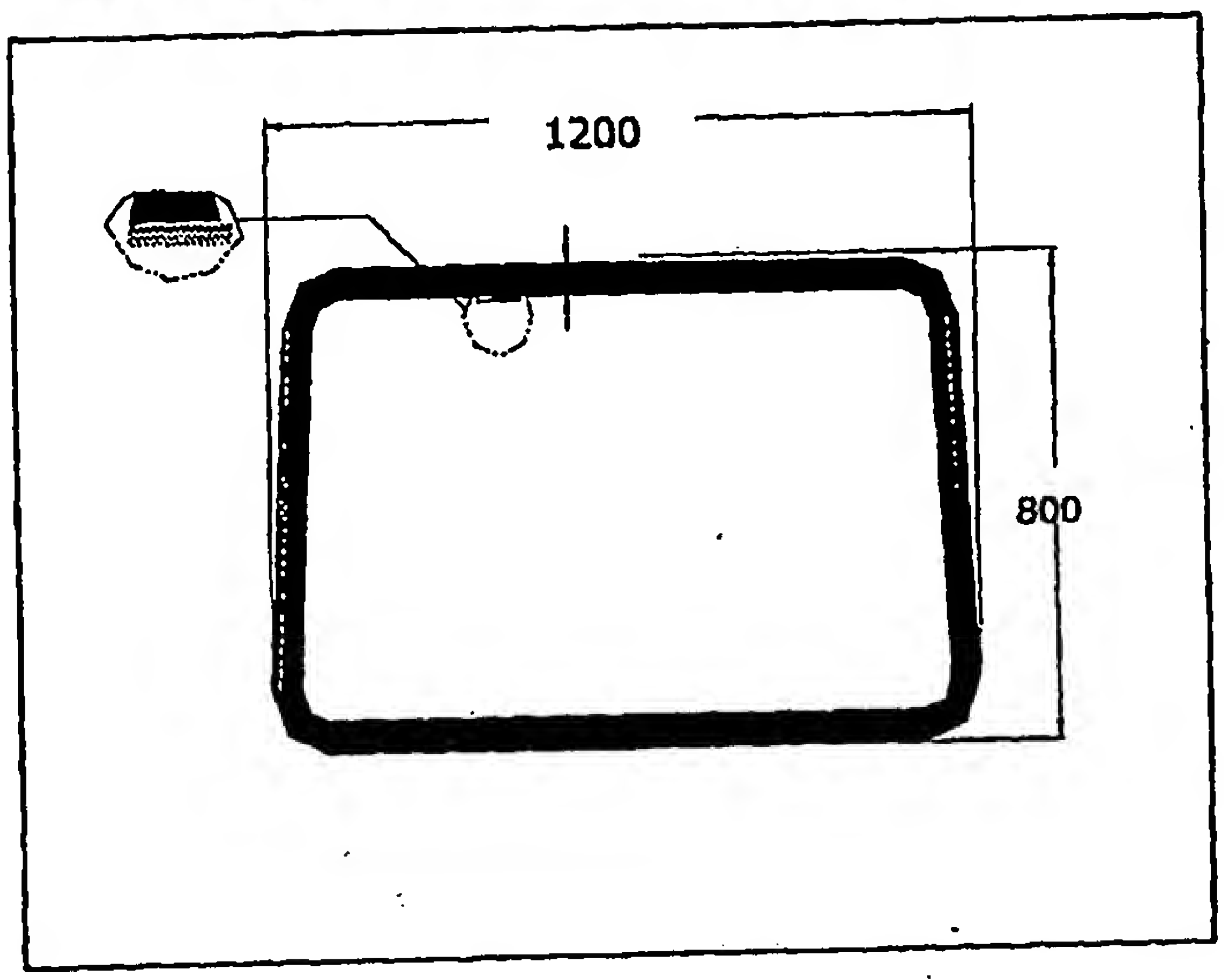
2.4 Drying/Curing system

One of the advantages of the digital printing is that during the printing, the drying process is taking place by means of Infrared or hot air; this feature of drying will save the use of IR oven that is required in the traditional screen-printing. (Clarification: the oven pre dries the glass to about 150°C, just for handling. The furnace of 630°C, which converts the glass into a safety glass, takes place later on in the process)

2.5 Software

The software deals with the special needs of printing as described in this document. The software also replaces the use of mechanical elements for printing on glass.

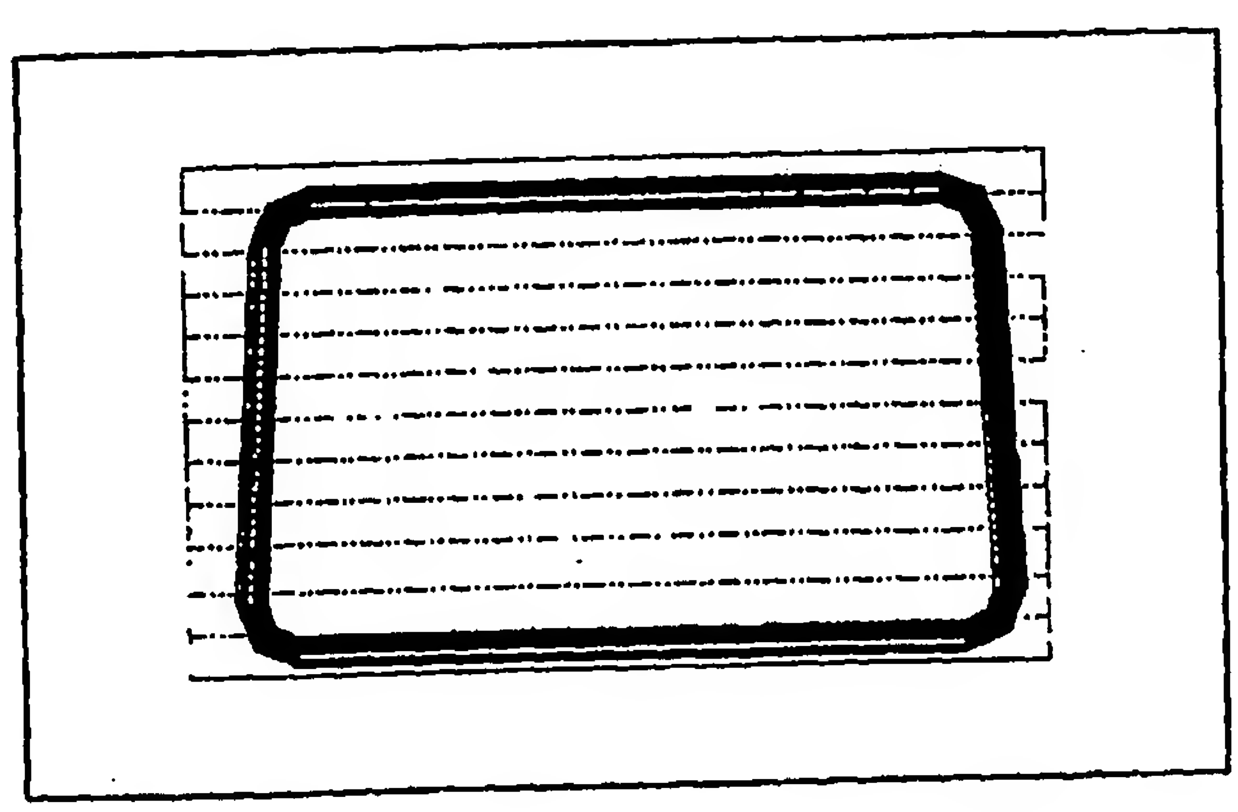
Typical pattern of car windshield



Printing methods that will be used in the new printer:

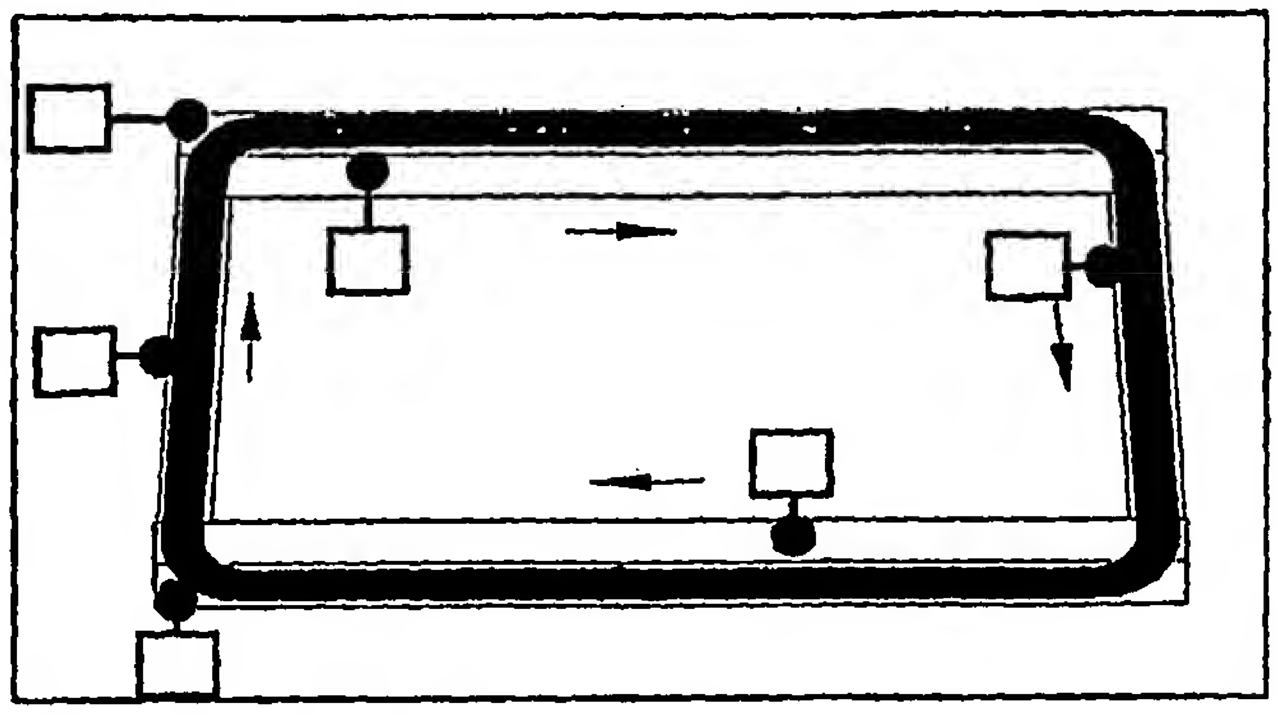
Traditional method of digital printing:

The print heads cluster sweeps the glass from side to side and paint the glass, some like paint brush.



Tile printing method

The pattern is divided by the computer into four (or more) typical tiles. The print heads cluster is able to rotate by means of servomotor in order to match the angle defined by the computer. This method is more efficient and time saving because of skipping the uncolored areas.



Contour printing method

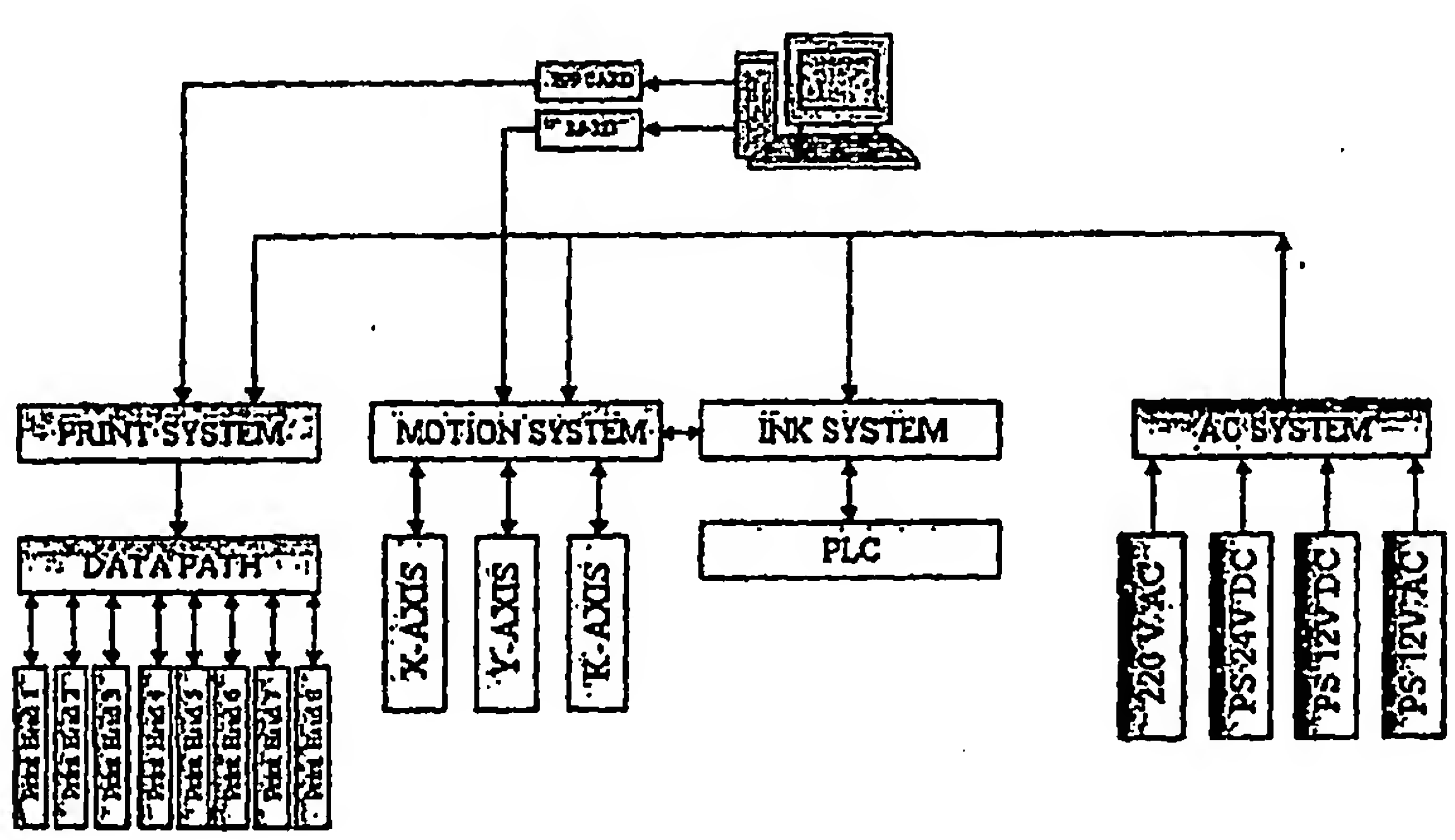
This printing method is also very useful. The computer defines the pattern contour. The print heads cluster is able to follow the track by X, Y axis and rotating axis of print heads cluster.

3. Outlet section

The printed glass is transferred from the printing section by means of vacuum cups gripping to the following process of the production line.

Block Diagram:

DGP SYSTEMS



III. The glass ink jet ink

This invention describes both solvent based and water based glass ink jet inks. In principle, the ink should meet the general requirements of an industrial ink jet ink (long shelf life, proper jetting, suitable patterns and line definition, fixation and adhesion on the substrate), and, in addition, the unique requirements resulting from its use, the printing on glass.

The use of conventional glass ink currently used in silk printing in ink jet printing is impossible. This is due to the very high viscosity of the silk printing ink, and due to the presence of micron size glass frit and pigment. As known in the art of ink jet printing, DOD and continuous ink jet print head can function only at very low viscosities (10-20 cps), and only with particles below 1 micrometer, preferably below 300-400 nanometers.

The special requirements related to glass printing (automotive and appliances and architectural industries) also prevent the use of conventional graphic arts ink jet inks for printing on glass. For example, at the high temperatures the glass is exposed to (above 600°C) while obtaining the required shape of the automotive glass, conventional black pigments will be burnt out and the ink would become transparent. However, since in commercial inks the binders are organic polymers, they would also be burnt out, thus leaving no pattern on the glass surface.

Therefore, this invention provides a glass ink jet ink, which can be fired at high temperatures, after printing, and become an integral part of the glass substrate. This is achieved in the present invention, by using sub micron black inorganic pigments together with a binder, which is in itself a glass forming composition (termed here "glass ink jet ink").

Therefore, in principle, after printing the glass ink jet ink on a glass surface, by a suitable ink jet printer, the glass with the printed pattern is fired at 500-650°C, thus forming a thin black pattern which is strongly adhered to the glass substrate, and in a way, the printed pattern becomes an integral part of the glass pattern. Therefore, the properties of both the glass binder and the pigment should be suitable for use in ink jet printer, and should have sufficiently low sintering temperature, in order to bring good binding to the glass surface.

The present invention indeed describe compositions and methods of preparation of glass ink jet ink which meet both requirements of the ink jet printing method, and the requirements of the automotive and architectural glass industries, as well as other industries requiring printing on glass, such as white color decorations on ovens windows.

Two types of compositions can achieve the glass ink jet ink of this invention:

1. Solvent based ink, in which the pigment is composed of inorganic metal oxides, and the binder is a glass frit, both in the sub micron size range.
2. Water based ink, in which the pigment is composed of inorganic metal oxides, and the binder is composed of: colloidal silica particles, organic polymer, and additives, which lead to a glass forming composition at temperature below 650°C.

Both types of compositions may contain, in addition to the pigment and the binder composition, suitable additives such as wetting and dispersing agents, defoamers, humectants, rheology control agents, anticorrosive agents, coalescent agents, pH control agents and biocides. If a rapid fixation on the substrate is required, a UV polymerizable composition can be also included in the glass ink jet ink, which would cause, if exposed to UV light immediately after jetting, a "freezing " of the droplets on the glass substrate.

Glass ink jet ink compositions

Both types of inks contain the following components: sub micron pigments, "glass binder composition", and a liquid vehicle (solvents and/or water).

Since the pigments are the same for both types of inks, their properties and methods to achieve them will be described separately in the following section:

Pigments

One common component of both types of glass ink jet ink is the sub micron, heat resistant pigments. Although in this invention we describe a black ink, the invention can be easily applied to pigments having other colors. These pigments can be oxides of metals such as chromium oxide, cupper oxide or mixed oxides $CuCr2O3$ (for black color), titanium dioxide (for white color) etc._Important feature of the pigments, in order to be suitable for ink jet printing, is the requirement of very small size of the pigment. Conventional pigments, which are currently used in the automotive industry by silk printing, are in the micrometer size range, which is unacceptable for ink jet printing. Therefore, the required pigment size may be obtained either by milling and grinding the micron size pigments (by suitable instruments such as ball mill, pearl meal, jet mill etc.), or by synthesizing the pigment in conditions yielding sub micron particles (such as solution precipitation, forced hydrolysis, from metal alkoxides, reaction in gas phase etc.). It should be emphasized that in the two types of glass ink jet inks described in this invention, the pigment should provide, after printing and firing at high temperature, suitable optical properties, such as optical density, UV blockage, gloss etc.

Proper selection of the pigment/binder ratio, concentration of the pigment in the ink, and the particle size distribution of the ink can achieve these optical properties.

A. Solvent based glass ink jet ink

The binder in this glass is a glass frit, milled to yield particles size below 0.9 micrometers. The glass frit composition is selected such that the glass would have sintering temperature below 600°C, and low thermal expansion (below 90x10-7/K). The glass frit is composed of: SiO_2, Bi_2O_3, B_2O_3, in a decreasing molar concentration order. The exact composition can be tailored according to the required melting temperature, degree of crystallinity, thermal expansion and chemical resistance. Typically, the molar concentration ranges of these components are: 50-70%, 10-20% and 3-20%, respectively.
The sub micron particles were obtained by wet milling of a micron size frit powder, dispersed in Dowanol DB, in presence of a dispering agent.

The pigment in this formulation was also prepared by wet milling of Cr-Cu –oxide micron size pigment, dispersed in Dowanol DB in presence of a dispersant. The pigment particles were below 0.7 micrometer, while 90% of the particles were below 0.4 micrometer.
The resulting dispersions of the sub-micron glass frit and pigments were mixed in such a proportion to yield 3:1 weight ration of frit particles to pigment particles. The dispersion was further diluted with Dowanol DB, and additional solvents (TPM, PMA), and a dispesant is added, to yield low viscosity ink, having 46.5 % solids content.

Preparation Procedure:

Add pigment dispersion, cosolvent (TPM or PMA) and Disperbyk-163 to frit and mix by Dispermat for 5 min after each material addition. Then, add Dowanol DB during mixing and mix again by Dispermat (30 min, 9000 rpm).
The resulting inks were filtered through 1-micrometer filter, without clogging the filter, and without significant change in the solids content.
For initial testing, the samples were applied on glass as 5 ul drop and dried in a furnace at 650 °C during 1 hour.
Further tests were performed by jetting the ink at 45°C or 55°C, temperature in which the inks viscosities are about 11cps. The exact composition and properties of two ink jet inks are presented in the following table.
In general, it was found that the overall performance of the ink in the ink jet print head (Spectra) was very good (jetting, line definition, jetting reliability, no print head clogging), and that the printed pattern has gloss and good optical density after firing at 650°C.

The chemical resistance was tested by immersion in solutions of sulfuric acid at 80°C, 4 hours, and NaOH solution overnight, and found to be excellent. Sample YL-20-5 was tested for several days while in the print head, and it was found that even after a prolonged shut down, a simple purge and wiping of the orifice plate, led to immediate printing and full performance of the print head.

Sample Name	Composition	% Solids	Viscosity, at 45° C	Viscosity, at 55° C	Surface tension, mN/m	Particle size in composition, nm (HPPS, by volume)
YL-20-5	Frit IJFRIT2N – 57.89 g Pigment IJBLAC2D– 19.3 g TPM (10% wt) – 8.57 g Disperbyk-163 (1% wt) – 0.87g Dowanol DB – 34.62 g (dilution 1.4 times)	46.5	11.9	-	26.1 ± 0.05	100% below 530 nm
YL-22	Frit IJFRIT2N – 57.89 g Pigment IJBLAC2D– 19.3 g PMA (10% wt) – 8.57 g Disperbyk-163 (1% wt) – 0.87g Dowanol DB – 34.62 g (Dilution 1.4 times)	46.5	14.2	11.6	25.0 ± 0.03	100% below 718 nm

The properties of the sub-micron frit are given in the following table:

Technical Data for Glass Frit IJFRIT2N

Characteristics	Specification
Chemical Composition	Bismuth borosilicate; Li-containing; Pb: < 1000 ppm Cd: < 50 ppm Bi_2O_3: (62±2) % (w/w)
Glass transition temperature T_g (measured by DSC as inflection point)	(479±5) °C
Linear coefficient of thermal expansion (20-320 °C)	(7.8±0.4) ppm/K
Chemical resistance 0.1N H_2SO_4/80°C 0.1N NaOH/22°C 3.7% HCl/5 min	>4 hours >24 hours 4 (ASTM C724-91)
Particle size (by number)	D_{50} = 0.06 µm D_{90} = 0.11 µm
Particle size (by volume)	D_{50} = 0.14 µm D_{90} = 0.90 µm

B. Water based glass ink jet ink

This type of ink is contains as the liquid, mostly water, and as the glass binder, a mixture of glass forming material and an organic polymer. The glass forming material described in this invention is based on silica nanoparticles (size below 100 nanometers), and water soluble materials which causes a significant decrease in the sintering temperature of the silica, thus allowing good adhesion and glass formation by the silica particles, at as low temperatures as 580C.

The possible use of the silica nanoparticles overcomes the need for frit milling in order to obtain the required size of the glass forming materials. The present inventions thus provide a simple method and compositions to prepare low viscosity, heat and chemicals resistant glass inks, having only water-soluble materials together with nanoparticles. This type of inks is especially suitable for ink jet printing, due to the very low viscosity and small size of the particles.

The process for preparation of the ink is very simple: only mixing of the components is required in order to obtain homogenous, stable inks. More specifically, the glass forming binder is based on commercially available silica dispersions, such as the Ludox, produced by Du Pont.

It was found, in general, that by applying the Ludux dispersions on glass, followed by firing at temperatures below 650°C, all Ludox dispersions, which were tested, did not form a glassy film on the glass substrate, and could easily peeled of. It was therefore obvious that the colloidal silica solutions by themselves are not suitable as glass binder at that low temperature.
We found that it is possible to dissolve in the Ludox dispersion specific electrolytes, which, in presence of organic polymers, could strongly bound to a glass surface, giving an acid and base chemical resistance.
The organic polymers (water soluble or colloidal system) and the water soluble additives should be carefully selected, since it appears that optimal performance of the glass binder can be achieved only with limited classes of additives. Therefore, we were able to use such compositions as the binder component in the water based glass ink jet ink.

The following section shows some specific examples of compositions of Ludox based glass binder systems, which gave good adhesion to glass, and high chemical and heat resistance.

<u>Water- based formulations of "Glass forming solutions"</u>

Formulation with Joncryl-95 (5.1 % SiO_2 as solids) without pigment

	Wt. of solution, g	wt. of solid, g
• Ludox TMA solution	1.00	0.34
• Sodium perborate tetrahydrate (1.6%) sol.	4.03	0.065
• Joncryl – 95	0.28	0.084
• Glycerol	0.33	0.33
• Dowanol DB	1.00	1.00
• BYK-348	0.0053	0.0053

Formulation with PVP (4.99 % SiO_2 as solids) without pigment

	Wt. of solution, g	wt. of solid, g
• Ludox TMA solution	1.00	0.34
• Sodium perborate tetrahydrate (1.6%) sol.	3.62	0.058
• PVP (30%) sol.	0.83	0.25
• Glycerol	0.34	0.34
Dowanol DB	1.02	1.02
• BYK-348	0.0068	0.0068

Procedure:

Add Joncryl-95 (PVP) to Sodium perborate solution and mix by stirrer for 5 min. Then, add Glycerol, Dowanol DB and Ludox solution with mixing (5 min) after each addition. The BYK-348 is added last and mix again (5 min).

Formulation with PVP and Aluminum phosphate (9.2 % SiO_2 as solids) without pigment

	Wt. of solution, g	wt. of solid, g
• Ludox TMA solution	1.00	0.34
• PVP (15.0%) sol.	1.67	0.25
• Aluminum Phosphate sol.	0.30	0.15
• Glycerol	0.37	0.37
• Dowanol DB	0.37	0.37
• BYK-348	0.0037	0.0037

Procedure:
Add Glycerol and Dowanol DB to PVP solution and mix by stirrer for 5 min after each material addition. Then, add Ludax and mix again (5 min). The Aluminum Phosphate solution was added after Ludox while stirring. The BYK-348 is added last and mix again (5 min).

Formulation with Joncryl and boric acid (12.7 % SiO_2 as solids) without pigment

	Wt. of solution, g	wt. of solid, g
• Ludox TMA solution	1.00	0.34
• Sodium perborate tetrahydrate (1.6%) sol.	1.00	0.016
• Boric acid	0.024	0.024
• Joncryl-95	0.28	0.084
• Glycerol	0.17	0.17
• Dowanol DB	0.52	0.52
• BYK-348	0.0034	0.0034

All samples were applied on glass as a 5ul drop and fired in a furnace at 650°C during 1 hour. The resulting coating was scratch resistant, and withstands soaking in acid and base, in a testing procedure similar to that of the solvent based frit glass inks described earlier.

Once having the water soluble glass binders, it was possible to prepare glass ink jet inks, simply by mixing a pigment dispersion with the glass forming binder.

Such compositions are described in the following section.

Formulation with Joncryl-95 (with 15%wt pigment from formulation)
(4.1 % SiO_2 as solids)

	Wt. of solution, g	wt. of solid, g
Ludox TMA solution	1.00	0.34
• Sodium perborate tetrahydrate (1.6%) sol.	4.03	0.065
• Joncryl – 95	0.28	0.084
• Glycerol	0.33	0.33
• Dowanol DB	1.00	1.00
• BYK-348	0.0053	0.0053
• Pigment IJBLAC1J (sample Y-275-1)		
• Or Pigment IJBLAC2D (sample MA-20-2)	1.6	1.17

This formulation has a viscosity below 10 cps, and surface tension below 40 dynes/cm, making it an excellent candidate for ink jet printing. The formulation A unique and surprising feature of this ink is it's high chemical and scratch resistance, in spite the fact that the glass to pigment ratio is much lower than conventional paint and ink systems (in conventional glass ink for silk printing this ratio is 3:1, while in this ink the ratio is the opposite, 1:3.6.

Formulation with Joncryl and boric acid (with 15%wt pigment from formulation)
(9.6 % SiO_2 as solids)

	Wt. of solution, g	wt. of solid, g
• Ludox TMA solution	1.00	0.34
• Sodium perborate tetrahydrate (1.6%) sol.	1.00	0.016
• Boric acid	0.024	0.024
• Joncryl-95	0.28	0.084
• Glycerol	0.17	0.17
• Dowanol DB	0.52	0.52
• BYK-348	0.0034	0.0034
• Pigment IJBLAC2D (MA-20-2)	0.83	0.6

Based on our findings it appears that it is also possible to combine the Ludox type systems with water glass solutions, or even use water glass solutions only, and obtain interesting features of the ink after firing. For example one may obtain a porosive ink, by using the following ink compositions based on water glass:

Na-silicate based formulations of "Glass forming solutions"

Formulation without pigment (9.6 % SiO_2 as solids)

	Wt. of solution, g	wt. of solid, g
• Sodium silicate solution	9.99	2.50
• Glycerol	2.5	2.5
• BYK-348	0.013	0.013

Formulation with with 15%wt pigment from formulation (17.0 % SiO_2 as solids)

	Wt. of solution, g	wt. of solid, g
• Sodium silicate solution	9.99	2.50
• Glycerol	2.5	2.5
• BYK-348	0.013	0.013
• Pigment RM.658 UV	2.21	2.21

Procedure:

Add Glycerol and BYK-348 to Sodium silicate solution and mix by stirrer for 5 min after each material addition. Then, add pigment and mix again by Dispermat (15 min, 9000 rpm).

This low viscosity sample was applied on glass as 5 ul drop and dried in a furnace at 650 °C during 1 hour, and gave a porosive coating, which was strongly adhered to the glass substrate.

In conclusion, this part of the invention describes compositions of inks, which have the ability to strongly adhere onto glass substrates, yielding excellent performance after printed and fired at temperatures as low as 580 C.

Obviously, as described in this invention, once the basic low viscosity glass ink jet ink can be obtained, it is possible to modify the ink compositions according to the required application. For example, one may increase the solid content, in order to obtain thicker patterns, one may change the components in order to yield an ink which has high viscosity at room temperature and low temperature at the jetting temperature (in order to prevent settling of the pigment or frit particles), or one may add polymers or increase the solid content in order to obtain a pseudoplatic behavior, or, one may add monomers, oligomers and photoinitiators, which can be polymerized upon exposure to UV light thus casing rapid fixation of the jetted ink droplets immediately after contact with the glass substrate.

It is clear to a person skilled in the art of coating technologies that the above water-based formulations are suitable for application in coating applications other than ink-jet printing. This type of ludox containing water-based formulation can be easily adapted to applications other than printing on glass, such as tile, ceramic and micro-electronic applications.